QUALITY-CONTROL SAMPLES 4.3

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Collection of quality-control (QC) samples is a required component of sample collection for water-quality studies. QC samples are collected, usually at the field site, in order to identify, quantify, and document bias and variability in data resulting from the collection, processing, shipping, and handling of samples by field and laboratory personnel. **The bias and variability associated with data must be known so that environmental data can be adequately interpreted** (Horowitz and others, 1994; Koterba and others, 1994; Koterba and others, 1995).

The procedures for collecting QC samples can depend on, or be modified according to, the purpose of the quality-assurance program. Thus, personnel need to understand the purpose for each QC sample to be collected (Appendix A4-B) and how the resulting QC data will be used. The type, number, and distribution of QC samples are determined by the design and data-quality requirements of the study. For any water-quality sampling schedule, personnel must:

- **Be aware that an equipment blank is required at least annually (NFM 3).**
- **Be alert to field conditions** for which blanks or other QC samples should be collected, in addition to those planned. **It is usually best to collect the additional QC samples;** it can be decided later whether to submit them for laboratory analysis.
- **Collect all field QC samples on the same day that environmental samples are collected,** using the same equipment as for environmental samples.

- **Obtain the QC sample solutions needed.**
  - Blanks. The source solution needed for blank samples must be produced and certified by a laboratory to have analyte concentrations that do not exceed a specified method detection limit. Review and keep on file the certificate of analysis for each lot of blank water; keep a record of the lot numbers used for each sample.
    - Inorganic-grade blank water (IBW) is required for blanks that will be analyzed for inorganic constituents.
    - Pesticide-grade blank water (PBW) and volatile-grade blank water (VBW) are required for blanks that will be analyzed for pesticides and volatile organic compounds, respectively. VBW can also be used for pesticide blanks.
    - VOC trip blanks must be requested from the laboratory as a separate order and can be shipped with an order for VOC vials.
  - Replicates and field-matrix spikes. The surface or ground water being sampled (environmental water) is the solution used for most types of replicates (sequential, split, and concurrent samples) and spikes.
  - Standards and reference materials. Standards and reference materials are either artificial or environmental solutions with known and certified analyte concentrations.
    - Reference materials usually are obtained from the National Institute of Standards and Technology (NIST) (http://www.nist.gov).
    - USGS personnel can obtain Standard Reference Water Samples (SRS) from the USGS Branch of Quality Systems (http://btdqs.usgs.gov).
- **Use preservatives from the same lot number** for the environmental and associated QC samples. Record preservative lot number.

- **Label QC sample bottles** with a QA sample-designation code, site identification number, date of sample collection, and an assigned or real time of collection. Identification of specific types of QC samples can follow a study-developed time-coding protocol in which a specific time interval is assigned that pertains only to a specific type of QC sample.
- **Store QC data in an electronic data base devoted to QC data.** For USGS studies, it is recommended that this be an alternative data base within NWIS QWDATA—check for District and (or) program protocols for QC data-storage requirements.

Use Good Field Practices (table 4-1) and Clean Hands/Dirty Hands techniques (table 4-2) when collecting and processing QC samples.

BLANK SAMPLES 4.3.1

The primary purpose of a blank sample is to identify potential sources of sample contamination and assess the magnitude of contamination with respect to concentration of target analytes (Appendix A4-B). There are many possible types of blanks, and the processing procedures described below and in Appendix A4-B address only those most commonly collected. (Additional information can be found in Branch of Quality Systems memorandums 92.01 and 95.01; Sandstrom, 1990; Horowitz and others, 1994; and Koterba and others, 1995, although terminology differs somewhat among these references.) Examples to estimate the volume of blank solutions needed for field QC and blank-collection protocols are given in Appendix A4-C.

4.3.1.A Source-Solution, Equipment, Trip, and Other Prefield Blanks

Prepare the source-solution blank, equipment blank, and trip blank before going to the field for environmental sampling. Wear gloves and conform to other clean-hands practices when working with blank solutions.

- **Source-solution blank.** Collect in a designated clean, draft-free area of the office laboratory, such as under a laminar-flow hood or laminar-flow bench. **Do not collect the source-solution blank in a fume hood.** Submit the sample for analysis along with field-collected samples.
- **Equipment blank.** Collect in a designated clean area of the office laboratory. Collect the equipment blank at least 4 weeks before using the equipment in the field to ensure enough time for chemical analysis and review of the resulting QC data.
- **Trip blank**. Carry the trip blank as received from the laboratory to the field site. Do not open, but store with the environmental samples collected for the same target analytes, and submit for analysis along with the field-collected samples. Record the trip-blank lot number on the NWQL Analytical Services Request (ASR) form submitted with the vial. (The lot number can be found on the box, and is sometimes printed on the label.)

A variety of other types of blank samples that are collected in the controlled office-laboratory environment can be designed to test some aspect of sample handling not related to field activities. Examples of this type of blank (described in Appendix A4-B) include the refrigerator blank, the shelf blank, and the preservation blank.

When working with blank water, wear disposable, powderless gloves and implement clean-sampling techniques.

Ambient and Field Blanks 4.3.1.B

The collection of blank samples, described in this section, addresses onsite (field) processing of blank water in the same environment in which the surface- or ground-water samples are collected and (or) processed.

To prepare for processing blank samples:

1. Label the capped, precleaned sample bottle with the site identification number, laboratory sample designation code (NFM 5), date, and time.
2. Put on gloves. Place each stock container of the blank solution to be used into clean plastic bags.
    - IBW—Required for trace-element, major-ion, and nutrient field-blank analysis.
    - PBW—Required for pesticide field-blank analysis; can be used as a blank for total or dissolved organic carbon (TOC/DOC).
    - VBW—Required for VOC field-blank analysis; can be used as a blank for TOC/DOC and pesticides.
3. If pumping blank water from a standpipe, change gloves and then rinse the precleaned standpipe three times using a small volume of blank solution of the type selected. Keep standpipe covered until use.
4. Change gloves. Place precleaned, labeled sample bottle(s) and the stock of blank solutions to be used into processing chamber.
    - IBW blanks—Discard the deionized water that half fills the precleaned polyethylene sample bottle. Rinse the sample bottle with a small quantity of blank solution and discard rinsate before filling with IBW.
    - PBW or VBW blanks—Do not prerinse the sample bottle. Use glass bottles or vials as received precleaned from the laboratory.

Ambient blanks

Ambient blanks are used to answer questions such as "To what extent could exposure of the sample to its collection and processing environment introduce measurable concentrations of target analytes?" Depending on the site characteristics or conditions being subjected to quality control, different procedures can be used for collecting the ambient blank. Three common procedures are described below. For each procedure, prevent contamination of the source solution and blank sample by capping the respective bottles immediately after use.

Procedure 1. Fill clean sample bottle(s) with the appropriate blank water in the same office-laboratory area in which the source-solution blank is collected, and transport to the field. Place the bottle(s) in the processing or preservation chamber or other area in which the environmental sample(s) are being processed. Open the blank-sample bottle to expose blank sample to the chamber atmosphere for the period of time in which the environmental sample(s) are being processed. Cap the bottle(s) and label appropriately.

Procedure 2. Working within the area being tested (usually the area in which the environmental sample is being collected or processed), pour blank water from the source-solution container directly into the sample bottle. Cap the bottle immediately and label appropriately. The goal is to use similar procedures to expose an identical volume of blank water to the ambient atmospheric conditions as that for collection of sample water.

Procedure 3. While working within the area being tested (such as a field vehicle), fill a clean, wide-mouthed container with the type of blank water desired and leave open to the atmosphere for the entire testing period. Pour the blank water into a clean sample bottle. Cap the bottle and label appropriately. (This type of ambient blank is sometimes referred to as an atmospheric blank.)

Field blanks

Field blanks are collected and processed at the field site in the same manner and using the same equipment as the environmental sample(s). Equipment must be meticulously cleaned for collection of field blanks (NFM 3). Field blanks answer questions such as "Has this component of the equipment system been adequately cleaned?" or "Does this equipment component introduce detectable concentrations of target analytes?" or "Is there carry-over contamination from the previous sampling site?"

- Field blanks can represent equipment components of the sampling system; for example, the sampler blank, splitter blank, filter blank, or pump blank. (The pump blank for ground water often is the same as or analogous to a sampler blank, when a pump is the type of sampler used to withdraw water from its original source.)
- A single field blank that represents the entire sampling system is commonly referred to as the field blank or field-system blank (fig. 4-8 and Appendix A4-B). The field blank is comprised of an aliquot of blank water processed sequentially through each component of the sampling system.

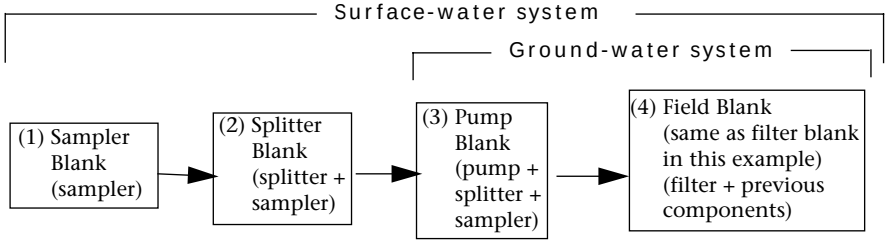
Submit field blanks for laboratory analysis of the same target analytes as the environmental sample(s). If the analytes being quality controlled are inorganic, preserved with acid, and are not time dependent, the sequential blank samples representing components of the sampling system and any associated source-solution and ambient blanks normally can be stored for up to 6 months.

1. If the field-blank data indicate constituent concentrations at acceptable levels, the associated set of sequential blanks can be discarded. (Be sure to use appropriate means for disposing of chemically treated solutions.)
2. If laboratory data indicate greater than acceptable concentrations:
   a. Submit the source-solution blank, ambient blank(s), and equipment-component blank(s) (the sampler blank, splitter blank, pump blank, and so forth) to the laboratory for analysis.
   b. Use the data from equipment-component blank samples to identify the source(s) of contamination detected in the field blank.
   c. Take appropriate measures to eliminate contamination during future sampling trips.

EXAMPLE PROCEDURE FOR COLLECTING FIELD BLANKS

A set of blanks can be generated that is associated with the field blank to help determine which equipment component in the system could be a source of contamination. The field blank is the final sample that represents all equipment components of the sampling system. After each blank sample is collected, preserve and store sample as required.

- **Follow steps 1 through 4 to process a surface-water field blank.** In this example, the equipment used includes a US D-77 sampler, 8-liter (L) churn splitter, peristaltic pump, and filter assembly.
- **Follow steps 3 and 4 to process a ground-water field blank.** In this example, the equipment used includes a submersible pump and a filter assembly.



(1) Sampler Blank. Using the blank water selected, rinse and then fill the sampler; attach sampler cap and nozzle; pour the required volume through nozzle into sample bottle.

(2) Splitter Blank.[1] Rinse churn splitter with blank water. Pour the blank water remaining in the sampler through the sampler nozzle and into the 8-L churn splitter. Refill sampler, repeat until churn contains 3 to 5 L of blank water. Process the required blank-sample volume through the churn spigot into the splitter-blank bottle. (If a cone splitter is used instead of a churn splitter, the blank sample is processed through the exit port tubes.)

(3) Pump Blank.[1]

- **Surface-water example**: Using the peristaltic pump, thread the intake end of clean tubing into churn splitter through the funnel, and cap the funnel loosely. Insert the discharge end of the pump tubing into a processing chamber and pump blank water through the tubing for an initial rinse, discharging rinse water to waste. After the rinse, pump the required volume of blank water from the churn splitter into the pump-blank bottle.
- **Ground-water example:** Rinse a precleaned, noncontaminating standpipe with blank water and discard rinse water. Place submersible pump into the standpipe and pour in blank water—keep water level above the pump intake. Insert discharge end of pump tubing into a processing chamber. Circulate blank water through pump and tubing to rinse, discharging rinse water to waste. Pump the required volume of blank water from the standpipe into the pump-blank bottle.

(4) Field-System Blank (the field blank). The **field blank** in this example is the same as a special type of **filter blank**[1] because the filter assembly is the final component of the equipment system through which the blank is processed. Working in the processing chamber, precondition the filter with blank water (NFM 5).

- **Surface-water example:** Pump the required volume of blank water from the churn splitter through the prerinsed filter assembly into the field-blank bottle.
- **Ground-water example:** Pump the required volume of blank water from the standpipe through the prerinsed filter assembly into the field-blank bottle.

[1]These are special cases of a splitter blank, pump blank, and filter blank, respectively, because the equipment component named is the final component but not the only component contacting the blank sample.

Figure 4-8. Example of procedure for collecting field blanks and associated blank samples.

REPLICATE SAMPLES 4.3.2

The primary purpose of replicate samples is to identify and (or) quantify the variability in all or part of the sampling and analysis system. Replicates—environmental samples collected in duplicate, triplicate, or higher multiples—are considered identical in composition and are analyzed for the same chemical properties. Common types of replicates are described below.

Concurrent Replicate Samples 4.3.2.A

Concurrent replicates are simultaneously collected samples of environmental water used to answer questions such as "What was the variability introduced from collection, processing, shipping, and laboratory handling of the sample?" Concurrent replicates can be designed to assess variability inherent in the system being sampled (Appendix A4-B).

Depending on study objectives, concurrent samples can be collected by using two sampling devices of the same type simultaneously or by filling separate sample-compositing containers concurrently using the same sampling device. The following procedure (from Horowitz and others, 1994) is used at surface-water sites to fill two or more sample-compositing containers (usually churn splitters) and incorporates Clean Hands/Dirty Hands techniques:

1. Complete equipment field-rinsing procedures (section 4.0.2). Label bottles appropriately. Change gloves.
2. At the first vertical of an EWI or EDI section, collect a sample and pour into a field-rinsed churn splitter (section 4.1).
3. Resample the first vertical and pour into the second churn splitter.
4. Move to second vertical, collect sample, and pour into second churn splitter.
5. Resample second vertical and pour into first churn splitter.
6. Collect and pour sample into each churn splitter in this manner for each of the remaining verticals, alternating churn splitters as described in 2-5 listed above.
7. Process and preserve a sample (a) from the first churn, and (b) from the second churn.

4.3.2.B Sequential Replicate Samples

Sequential replicates are samples of environmental water that are collected consecutively instead of simultaneously. Sequential replicates are used to assess variability among samples resulting from collection, processing, shipping, and laboratory procedures conducted at different sampling times. The sequential replicate can be designed to assess sample variability from inhomogeneities in the system being sampled by spacing samples over short or long time periods.

4.3.2.C Split Replicate Samples

Split replicates are samples that are divided into two or more equal subsamples, each of which is submitted to one or more laboratories for the identical analysis. Field-split samples are used to assess variability from sample processing and preservation. Bottles must be appropriately labeled, and the sequence of procedures used must be recorded.

To split a sample into two subsamples after the original has been processed and preserved, use the following procedure (from Horowitz and others, 1994):

1. Wearing disposable, powderless gloves and working inside a processing chamber, start with a full sample bottle of processed (whole-water or filtered) sample.
    - For inorganic samples only, use a bottle rinsed twice with deionized water and then field rinsed with a small volume of processed sample.
    - Do not field rinse bottles for organic samples.
2. Transfer entire contents of first bottle to second bottle, cap second bottle, and thoroughly shake bottle to mix.
3. Pour entire contents of second bottle back into first bottle.
4. Pour one-half of sample from first bottle back into second bottle, then cap both bottles.

To split concurrent replicate samples that were processed through separate compositing devices (such as churn splitters), follow the procedure listed in 1-4 above and label the samples as follows (from Horowitz and others, 1994):

Churn splitter #1: first bottle "Site (X), Sample 1, Split A"
"Site (X), Sample 1, Split B"

Churn splitter #2: first bottle "Site (X), Sample 2, Split A"
"Site (X), Sample 2, Split B"

SPIKE SAMPLES 4.3.3

Spike samples are used to answer questions such as "What loss or gain of target analytes occurred because of water-matrix characteristics; the field processing, shipping, or handling procedures used; holding time; or laboratory analytical procedures?"

Typically, spikes are applied to samples to be analyzed for concentrations of organic compounds. A sample is spiked by adding a mixture of target compounds obtained from the laboratory to an environmental sample after the sample has been processed. **An unspiked environmental sample must accompany each spiked sample.**

Training is required before personnel attempt to spike samples. The spike kits provided to USGS personnel by the NWQL include the spike solution, equipment, and bottle labels, and detailed instructions.

The numbers and types of matrix spikes used depend on the objectives and data-quality requirements of individual studies, as determined by the project chiefs. Although analyses for a set of spike samples—laboratory spike, field spike, and field-spike replicate—provides the most complete information relating to the performance of the analytical method, the data from only laboratory spikes, or perhaps only one field spike, could be sufficient to meet study needs.

When preparing field-spiked samples for pesticides or VOCs, follow the procedure listed below:

1. Keep samples chilled until spiking. Label bottles appropriately.
2. Wearing gloves, spike each of the QC samples with the appropriate volume of the correct NWQL-provided spike solution:
   - Check that the pesticide samples are being spiked with pesticide-spike solution.
   - Check that the VOC samples are being spiked with VOC-spike solution.
3. Chill field-spiked samples to 4 °C or below without freezing, and handle in a manner identical to that of the environmental sample.
4. Record the following information related to the spike sample on field and NWQL Analytical Services Request forms:

   Lot number of spike solution, volume of spike solution, and source of spike solution.

4.3.4 REFERENCE SAMPLES

Standard-reference-water samples (SRS) and reference-material samples are used to answer questions, such as "What are the bias and variability associated with field-handling, shipping, and laboratory procedures?" Reference samples commonly are submitted from the field as blind samples (section 4.3.5) and as split replicate samples (section 4.3.2.C) because the composition is known, eliminating guesswork regarding the accuracy and correctness of the analytical results.

Reference samples with a natural water matrix are currently available to USGS personnel from the USGS Branch of Quality Systems. NIST and some commercial laboratories also supply reference materials.

When preparing reference samples, follow the procedure listed below:

1. Prepare this sample before leaving for the field site.
   a. Relabel the reference-sample bottle with the site identification code and a field date and time. The sample should appear as if it is an environmental sample.
   b. Process SRS or reference-material samples in a clean environment in the office laboratory, under a laminar-flow hood or other protective chamber, to avoid atmospheric contamination. Do not process these QC samples under a fume hood.
   c. Rinse each sample bottle three times with a small volume of SRS or reference-material sample, fill the bottle with the reference solution, and cap securely.
2. Prepare an ASR form; record the SRS or reference-material sample identification code (from the original container) in field notes.
3. Pack the sample and the accompanying ASR form to take to the field site.
4. Ship SRS or reference-material samples in the same container with the environmental and other QC samples collected at the field site.

BLIND SAMPLES 4.3.5

The source and chemical composition of blind samples are known to the submitter although typically not known to the analyst; therefore, blanks, SRS, or reference material usually are used as blind samples. Blind samples can be designed to answer questions such as "What bias and variability are introduced by procedures used within a single laboratory or among laboratories?" Replicate or spike samples also can be used to answer a similar question.